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(54) BLEACHING OF WASTE PAPER PULP

(71) We, HOOKER CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of New York, United States of America, of Niagara Falls, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for bleaching waste paper pulp to a commercially acceptable brightness in a single bleaching step.

With the increased awareness of the need for environmental stabilization, the recycling of waste paper has become an important issue. Heretofore, waste paper recycling processes have been deemed economically non-commercial owing to the relatively high cost of cleaning, de-inking, and bleaching thereof. Recently however technological advances have been made in the areas of commercial cleaning and de-inking processes which have provided a more economical and better grade of waste paper pulp. As a result, increased quantities of waste paper pulp have become available to the paper industry for recycling purposes, but, utilization thereof has been precluded by the high cost and complexity of equipment and chemicals necessary for bleaching by conventional methods.

High requirements are placed on the purity of the products obtained when manufacturing bleached, waste paper pulp. A large majority of the impurities found in the finished product originate from printer inks and dyes, pigments or discolored fiber bundles. The extent to which the pulp is freed from the aforementioned impurities depends partly upon how well the de-inking-cleaning operations are carried out.

There are many methods of de-inking and/or cleaning waste paper pulp. In one de-inking and cleaning process, old magazine stock, newspapers, broke, small quantities of groundwood (up to about 7%), and various waste papers containing a large number of coated cellulosic fiber materials, are first treated in any suitable manner to divide the paper into relatively small pieces. The paper is then subjected to a preliminary treatment with a solvent for the removal of, for example, resins, bitumin and tar, and also colored inks, by introducing the waste paper into a hopper and passing a solvent such as benzol, carbon tetrachloride, or trichloroethylene through the body of the paper, the solvent being recovered for re-use. Water is then added so as to form a dilute aqueous suspension, and various additives may be added, for example to reduce surface tension. The mass is then washed, screened, dried or otherwise prepared for storage prior to the bleaching processes.

As indicated above, the purity of the pulp depends upon how well the de-inking and/or cleaning operations have been carried out. Naturally economic factors limit the extent to which the pulp can be subject to purification by these means, and it has been shown in practice that a purified pulp, which has been subjected to the most careful de-inking and/or cleaning techniques, always contains a certain amount of color and impurities, mainly due to the presence of ink traces.

The principal intention, when bleaching waste paper pulp, is to increase the brightness of the pulp by oxidizing ink traces and other impurities, without appreciably lowering the viscosity of the cellulosic stock and with a minimal retention time in the bleaching apparatus. This is often effected by means of a sequence of bleaching stages, including treatments using, for example chlorine, hypochlorite, chlorine dioxide, or alkali. Oxidation of the impurities is most easily effected using discrete fibers which are more freely accessible to the influence of the bleaching chemicals.

It is apparent from the foregoing, that, in addition to expecting a brighter pulp from the bleaching process, a cleaner pulp is also anticipated, i.e. a pulp with less colored impurities than in the case of the unbleached pulp. In view of the present high requirements placed on the brightness of the bleached

pulp, the ability of the bleaching process to brighten the pulp is of great importance. In many cases as fed as 10 specks of insufficiently bleached impurities per square meter of sheet pulp may lead to such depreciation in the quality of the pulp that the pulp must be sold at a reduced price.

It has been known to bleach virgin cellulosic pulp with chlorine or chlorine dioxide, either separately or in a mixture. Chlorine bleaching of virgin pulp is usually effected at low temperatures (preferably below 70°F) and with low consistency (2.5—4.5%) and in short bleaching periods (30—90 minutes). The low pulp consistency is desirable for two reasons, firstly, to obtain a rapid, uniform intermixing of the chlorine in a pulp suspension which is necessary for obtaining a uniform chlorination of the pulp during the rapid reaction which takes place between the chlorine and lignin, and, secondly, to avoid sharp rises in temperatures in the pulp suspension owing to the strong exothermic reaction between chlorine and lignin, since high temperatures in chlorine bleaching lead to an uncontrollable oxidative decomposition of the pulp. Chlorine dioxide bleaching of virgin pulp is usually effected at high temperatures (80—180°F), higher consistencies (4.0—12.0%) and longer bleaching periods (3—6 hours) because of its lower oxidation potential. On the other hand, the bleaching of recycled, waste paper pulp has been limited in the prior art to chlorine or hypochlorite processes. Chlorine dioxide is considered a milder bleaching agent than chlorine or hypochlorite and the presence of difficult-to-bleach printer's ink and various other colored and paper coating impurities within the waste paper pulp reduce the effectiveness of chlorine dioxide as a bleaching agent. Further, in view of the presence of these difficult-to-bleach impurities, one would expect to utilize greater amounts of chlorine dioxide, at higher unit cost and longer bleaching time periods, to obtain a brightness approaching, but inferior, to that obtainable with Cl_2 or hypochlorite.

The present invention provides a process whereby recycled waste paper pulp can be bleached to a higher level of brightness, utilizing commercial viscosities, together with unexpectedly short retention times in the chlorinating apparatus, at a decrease in commercial cost in a single bleaching step wherein an aqueous mixture of the pulp is contacted with chlorine dioxide as the sole bleaching agent. The waste paper pulp is preferably contacted with up to about 1.0% by weight ClO_2, equivalent to about 2.64% Cl_2, so as to obtain a brightness of up to 92% (as determined by the standard TAPPI test) while maintaining a minimal viscosity change in the pulp stock. This demonstrates that ClO_2 is an effective bleaching agent for the treatment of waste paper pulp.

A wide temperature range is acceptable for the pulp suspension during the bleaching process. The temperature used would depend mainly upon the equipment available in a given mill. The process can be operated at relatively low or high temperatures, the process taking a shorter time at high temperatures and an extended time at low temperatures. The temperature range is preferably from 50°F to 180°F., depending on the mill equipment. A range of 140°F to 180°F., has been found to be particularly preferred. The heating of the pulp suspension may take place during or after its preparation by, for example, sparging in live steam or hot water.

The bleaching process is preferably conducted at a pH of about 2 to about 5, and most advantageously conducted at a pH of about 3 to about 4. While the pH of the aqueous pulp suspension should be maintained close to these stated ranges throughout the bleaching step, adjustment thereof may be accomplished before or concurrently with the addition of ClO_2 bleaching agent. The pH may be adjusted by the addition of acids, or of alkalis, such as caustic soda.

Despite the above described degrees of freedom in the matters of the timing and manner of adjustment of the pH, it has nevertheless been found somewhat advantageous to adjust the pH of the suspension preliminarily to certain specified values prior to the addition of the bleaching agent. The purpose of such preliminary adjustment of the pH is to ensure that as much as possible of the bleaching agent is consumed within the above mentioned ranges and, conversely, to ensure that as little as possible of the bleaching agent is flashed off under reduced pressure and wasted. Thus, the pH is preferably adjusted to about neutrality prior to the addition of the bleaching agent to the pulp suspension. Following the preliminary pH adjustment and the addition of the bleaching agent for the bleaching step, some further adjustment may be required to bring the suspension pH within the specified range for the bleaching process.

The waste paper pulp used in the bleaching process of this invention can conveniently contain up to 7% by weight groundwood.

Upon completion of the bleaching process the bleached pulp after a washing step, may be fed into the paper mill system together with normal pulp going to the paper machine. Due to the effectiveness of the bleaching process of this invention the bleached pulp can by dyed any color. Heretofore it was necessary to select a particular bleached pulp that could be used to furnish a particular color. This obviously, is of importance in regard to handling costs in quality control. The bleached pulp may also be stored in the aqueous or oven dried state for later use. The process of this invention displays a

further superiority over the prior art Cl_2 or hypochlorite processes in that later loss of brightness is less acute with the process of this invention as compared to the prior art.

The following examples serve to illustrate the invention; all parts and percentages are on a weight basis.

EXAMPLE I

Water was added to a quantity of oven dried, unbleached de-inked, commercial waste paper pulp so as to form an aqueous pulp mixture having a consistency of 3.5% cellulose fibers/96.5% water. The aqueous pulp mixture was then divided into separate samples, each sample with sufficient aqueous pulp mixture to contain 25 grams of the cellulosic fiber component. Viscosity, pH and Brightness were then determined using standard TAPPI tests with the following results:

Viscosity	15.1 cp
pH	7.0
Brightness	78.9

EXAMPLE II

A sample (containing 25 grams of the cellulosic fiber component) of the aqueous pulp mixture of Example I, was subjected to the following two-phase bleaching sequence:

First phase:

Sufficient 0.5 Cl_2/H_2O solution was added to a covered container, along with said sample, so as to form a solution therewith containing 0.3% Cl_2 calculated as weight percent of cellulosic fiber component. The solution was thereafter allowed to react, without agitation, at 80°F, for 10 minutes.

Second phase:

Immediately at the end of the 10 minute reaction time period of the first phase, 2.0% NaOH solution was added to the reaction product so as form a solution therewith containing 0.6% NaOH, calculated as weight percent of the cellulosic fiber component. The solution was thereafter allowed to react, without agitation, at 80°F, for 30 minutes

At the completion of the 30 minute reaction time period of the second phase, the pulp was tested using the standard TAPPI tests of Example I with the following results:

Viscosity	14.7
pH	11.2
Brightness	86.6

1 hour after the completion of the 30 minute reaction time period of the second phase, the pulp was tested for brightness using the standard TAPPI test of Example I with the following results:

Brightness	85.5

18 hours after the completion of the 30 minute reaction time period of the second phase, the pulp was tested for brightness using the standard TAPPI test of Example I with the following results:

Brightness	83.9

EXAMPLE III—X

Samples (containing 25 grams of the cellulosic fiber component) of the aqueous pulp mixture of Example I were subjected to the two phase bleaching sequence of Example II with the following modification and results:

	First Phase Reaction		Second Phase Reaction				Brightness		
	%Cl_2	Time	%NaOH	Time	Viscosity	pH	Final	1 Hr.	18 Hr.
Ex. III	0.3	10	0.6	60	14.8	11.3	87.7	86.6	84.8
Ex. IV	0.3	10	0.6	90	14.6	11.1	87.2	86.0	84.1
Ex. V	0.5	10	0.8	60	14.7	11.5	88.2	87.0	85.1
Ex. VI	0.5	10	0.8	30	14.7	11.4	86.6	85.6	83.9
Ex. VII	0.5	10	1.0	60	14.7	11.3	88.2	86.9	85.0
Ex. VIII	0.5	5	1.0	60	14.7	11.2	88.7	87.5	85.7
Ex. IX	1.0	5	1.5	60	13.8	11.0	88.5	87.0	85.1
Ex. X	1.5	5	2.0	60	13.3	10.2	89.1	87.4	85.4

EXAMPLE XI

Water was added to a quantity of oven dried, unbleached, de-inked, commercial waste paper pulp of Example I as to form an aqueous pulp mixture having a consistency of 4.0% cellulosic fiber/96.0% water the aqueous pulp mixture was then divided into separate samples, each sample having sufficient aqueous pulp mixture to contain 25 grams of the cellulosic fiber component. Standard TAPPI testing indicated that viscosity, pH and Brightness of the three samples were the same as in Example I.

A sample (containing 25 grams of the cellulosic fiber) of the aqueous pulp, as above prepared, was placed in a covered container, along with sufficient 0.5% ClO_2/H_2O solution to form a solution containing 0.114%

ClO_2 (equivalent to 0.3% Cl_2) calculated as weight percent of cellulosic fiber component. The solution was allowed to react, without agitation, at 160°F, for 180 minutes. At the completion of the 180 minute reaction time period, the pulp was tested using the standard TAPPI test of Example I with the following results:

Viscosity	14.4
pH	5.8
Brightness	90.4

1 hour, and 18 hours after the completion of the 180 minute reaction time period, the pulp was tested for brightness using the standard TAPPI tests of Example I with the following results:

	1 Hour	18 Hours
Brightness	89.5	87.7

EXAMPLES XII—XIII

Samples (containing 25 grams of the cellulosic fiber component) of the aqueous pulp mixture were prepared and bleached in accordance with Example XI with the following modifications and results:

	Equivalent To				Brightness		
	%ClO_2	%Cl_2	Viscosity	pH	Final	1 Hr.	18 Hr.
Example XII	0.19	0.5	14.4	5.4	90.4	89.8	88.0
Example XIII	0.38	1.0	13.7	4.3	90.7	90.0	88.7

WHAT WE CLAIM IS:—

1. A process for bleaching waste paper pulp in a single bleaching step which comprises contacting an aqueous mixture of the pulp with chlorine dioxide as the sole bleaching agent.

2. A process according to claim 1, wherein the pulp is bleached at from 50°F. to 180°F.

3. A process according to claim 2, wherein the pulp is bleached at from 140°F. to 180°F.

4. A process according to any one of the preceding claims, wherein the pulp is contacted with up to 1.0% by weight chlorine dioxide.

5. A process according to any one of the preceding claims conducted at a pH from 2 to 5.

6. A process according to claim 5 conducted at a pH from 3 to 4.

7. A process according to any one of the preceding claims in which the aqueous mixture of pulp is neutralised before it is contacted with the chlorine dioxide.

8. A process according to any one of the preceding claims wherein the waste paper pulp contains up to 7% by weight groundwood.

9. A process according to claim 1 substantially as hereinbefore described.

10. A process according to claim 1 substantially as described in any one of Examples XI to XIII.

11. Waste paper pulp whenever bleached by a process as claimed in any one of the preceding claims.

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